REPORT

H. Kawahata · I. Yukino · A. Suzuki

Terrestrial influences on the Shiraho fringing reef, Ishigaki Island, Japan: high carbon input relative to phosphate

Accepted: 20 February 2000

Abstract Measurements of CO₂ system parameters and nutrients showed the potential influence of terrestrial inputs on the carbon budget of a fringing coral reef on Ishigaki Island, Japan. Land-derived freshwaters, including river and ground water, make a relatively large contribution (0.5-1.2% by volume) to the water circulation of the reef. These terrestrial waters exhibit extremely high fugacity of CO₂ (fCO₂ up to 6400 µatm), reflecting enrichments in total alkalinity and dissolved inorganic carbon. Since the dissolved inorganic C:P ratio is anomalously high in terrestrial waters compared with the mean C:P ratios of primary production, excess carbon could be released into the atmosphere. Terrestrial inputs deliver a large quantity of C relative to P. The study site was a source of CO₂ at the time of measurement. Such a situation is likely to prevail all year round, and it may occur elsewhere.

Key words Carbon budget · Nutrients · Total carbon dioxide · Fringing reef · Ground water

Introduction

Coral reef flats are characterized by high rates of gross community primary production (mean 7 g C m⁻² day⁻¹; Kinsey 1985). Most organic matter produced is, however, consumed by community respiration. Consequently, the net community production by most reef flats is close to zero (0 \pm 0.7 g C m⁻² day⁻¹; Crossland et al. 1991). On the other hand, net community calcification (mean 10.8 g CaCO₃ m⁻² day⁻¹ on reef flats; Kinsey 1985) releases CO₂ into the water column, and

H. Kawahata · A. Suzuki Marine Geology Department, Geological Survey of Japan, Tsukuba, Ibaraki, 305-8567, Japan

H. Kawahata · I. Yukino Graduate School of Science, Tohoku University, Sendai, Miyagi, 908-8578, Japan the precipitated carbonate is stable due to its oversaturation in the surface water. Therefore, calcification plays a major role in the net carbon budget of coral reefs, where lagoonal water residence times are long enough for organic matter to be decomposed (Ware et al. 1992; Gattuso et al. 1993; Frankignoulle et al. 1994; Smith 1995; Suzuki et al. 1997). CO₂ evasions have been reported from the Fanning Atoll of the Line Islands (Smith and Pesret 1974), Canton Atoll in the Phoenix Islands (Smith and Jokiel 1978), Moorea in French Polynesia, Yonge Reef on the Great Barrier Reef (Frankignoulle et al. 1996; Gattuso et al. 1996a, b), and from the Palau Barrier Reef and Majuro Atoll in the tropical Pacific (Kawahata et al. 1997; Suzuki et al. 1997; Suzuki and Kawahata 1999).

Several recent papers, however, proposed that coral reef ecosystems are a sink of CO₂ on a fringing reef. Kayanne et al. (1995) carried out direct measurements of diurnal changes in fugacity of CO₂ (fCO₂) at a station on the Shiraho fringing reef during two 3-day periods. Because the mean fCO₂ value of reef water was lower than that of offshore water, it was concluded that coral reefs might serve as a sink for atmospheric CO₂. However, the extrapolation of this conclusion to a larger spatial/temporal extent has been criticized (Buddemeier 1996; Gattuso et al. 1996a). Yamamuro et al. (1995) analyzed $\delta^{15}N$ values of various organic materials from the same reef. Low $\delta^{15}N$ values of benthic primary producers indicated that primary production on the reef was accompanied by possible uptake of new nitrogen, which led to the conclusion that coral reef ecosystems are a sink for CO₂.

In this controversy of source or sink, one important aspect seems to be missing: the influence of terrestrial inputs. Especially in the case of a fringing reef, terrestrial inputs could play an important role because land-derived nutrients may enhance community primary production and lead to a decrease of fCO_2 in reef waters. The effect of terrestrial inputs on the community metabolism of coral reefs has received little attention so far. Here we present data on CO_2 in ground water, river

water, beach water, and reef water in the Shiraho fringing reef in order to evaluate the effect of terrestrial inputs on the net carbon budget of the fringing reef.

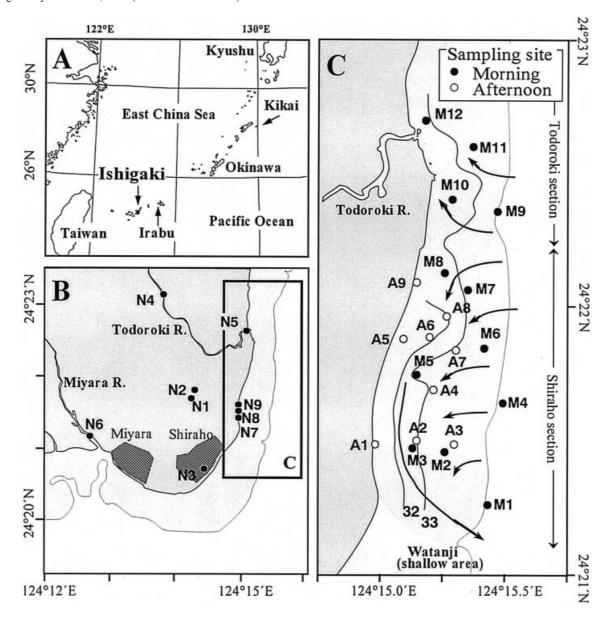
Study area

Ishigaki Island is situated at latitude 24°20′–24°36′N and longitude 124°05′–125°20′E in the southwest of the Ryukyu Islands, Japan. It lies in the path of the warm, nutrient-depleted Kuroshio current (Fig. 1A). Pleistocene reef carbonate sediments (Ryukyu limestone) are

Fig. 1 Location map of Ishigaki Island, Ryukyu Islands and the area studied on Shiraho reef (**A**). Sampling locations for ground water (Sts. N1–N3), river water (Sts. N4–N6), beach water (Sts. N7–N9) and reef water (Sts. M1–M12, A1–A9) around Shiraho area (**B**, **C**). Distribution of salinity with estimated general direction of currents was obtained using an automated self-recording salinometer during the morning survey of 23 June, 1997 (Kawahata et al. 1998)

widely distributed in the southern part of Ishigaki Island and are dominant in the Todoroki River catchments (Foster 1965). Field studies were carried out on the Shiraho and Todoroki sections of the Shiraho fringing reef situated on the southeastern coast of the island (Fig. 1B, C). Both sections contain well-developed fringing reefs about 800 m in width and 0–3 m in depth. The southern boundary of the Shiraho section is delineated by a shallow area called 'Watanji'. The reefs are classified into four topographic sub-areas based upon depth, gradient and surface roughness: (1) moat, (2) inner reef flat, (3) reef crest, and (4) outer reef slope.

The general circulation pattern of water on the reef flat was deduced from current measurements, arrangement of coral formations, and the distribution of sea surface temperature and salinity (Suzuki 1995; Kawahata et al. 1998). Offshore water enters the reef across the reef edge around the boundary between the Shiraho and Todoroki sections and flows landward



across the outer reef slope, reef crest and inner reef flat. The currents then turn south in the Shiraho section and north in the Todoroki section. The warmed water is drained offshore mainly through the depression to the north of 'Watanji'.

Materials and methods

Seawater and freshwater samples and temperature and salinity measurements were collected at 30 stations on 23 and 24 of June, 1997 (Fig. 1C). Offshore seawater samples were taken at Sts. M1 and M9. Ground water samples were taken at Sts. N1 and N2 in a cave, while ground water sampled at St. N3 near the coast was pumped up from a 10-m depth.

Methods for measurements of pH and total alkalinity (A_T) were similar to those described in Suzuki et al. (1997). The pH measurements at 25 °C (pH₂₅) were carried out in a laboratory within 4 h after sample collection, using a combined electrode radiometer (model GK2401C) with an ion-analyzer radiometer (model ION85). The pH measurements of two reference seawater samples taken at the same location immediately and 4 h after sampling showed <0.002 pH units difference. The electrode was calibrated with seawater scale (SWS) buffers (TRIS and AMP; Dickson 1993) before and after the series of measurements. The total drift was less than 0.3 mV emf. Readings of these buffers were quite uniform over 3 days.

Total alkalinity (A_T) of seawater passing through a GF/F filter was obtained by the potentiometric acid titration method, using a radiometer titrator (model VIT90). The precision and accuracy of the method are estimated to be 0.15% for A_T . A self-recording salinometer (MDS-CT, Aleck Electr. Co.) was used to measure salinity and seawater temperature with a precision of 0.04 and 0.05 °C, respectively. Concentrations of dissolved inorganic nutrients (phosphate and silica) were determined in water samples filtered through 0.45 µm acetate filters, according to the methods described by Strickland and Parsons (1972). Precision was 0.02 µmol kg⁻¹. Densities of all solutions were calculated from their salinity and temperature using the equation reported in Millero and Poisson (1981). Total CO_2 (C_T) and fugacity of carbon dioxide (fCO_2) were calculated from data sets of temperature, salinity, pH₂₅ and $A_{\rm T}$, using appropriate thermodynamic constants (Millero 1979; Weiss 1974). Other details are provided in Suzuki (1994, 1995), Suzuki et al. (1997) and Suzuki and Kawahata (1999).

Results

Offshore water

Two offshore water samples at Sts. M1 and M9 showed mean salinity, pH₂₅, $A_{\rm T}$ and $C_{\rm T}$ of 34.28, 8.080,

2246 μmol kg⁻¹ and 1980 μmol kg⁻¹, respectively, which were comparable to those reported previously by Suzuki (1995; Table 1; Fig. 2).

Reef water in the Shiraho and Todoroki sections

During the morning survey, the salinity and pH₂₅ varied from 32.96 to 34.33 and from 7.943 to 8.177, respectively, except at the Todotoki River mouth (M3, M5) where seawater was less saline and less alkaline due to freshwater inputs (Fig. 2A). $A_{\rm T}$ and $C_{\rm T}$ ranged between 2186 and 2784 µmol kg⁻¹ and between 1887 and 2535 µmol kg⁻¹, respectively (Table 1; Fig. 2B).

During the afternoon survey the salinity and pH₂₅ varied from 23.00 to 33.88 and from 8.014 to 8.514, respectively (Fig. 2B). Seawater near the beach showed lower salinity and lower pH₂₅. $A_{\rm T}$ and $C_{\rm T}$ ranged between 2056 and 3285 µmol kg⁻¹ and between 1676 and 2995 µmol kg⁻¹, respectively (Table 1; Fig. 2B).

Ground and river water

Ground water samples were relatively cool, around 24 °C, and pH₂₅ values were in the range of 7.318-7.493, which were the lowest among all the samples. All ground and river water samples had high $A_{\rm T}$ (2359 to 4189 μ mol kg⁻¹; average 3033 μ mol kg⁻¹) and C_T (2421 to 4362 μ mol kg⁻¹; average 3111 μ mol kg⁻¹; Table 2; Fig. 2A). These values were much higher than those observed in seawater on the reef flat. Nutrients, such as phosphate and silica, were as high as 1.22 μmol kg⁻¹ and 173 μmol kg⁻¹, respectively. The mean phosphate concentration of 0.66 μmol kg⁻¹ was in the range of those (0.19–0.93 µmol kg⁻¹) reported from interstitial water in the Ryukyu limestone at Irabu Island, on the Ryukyu Islands (Fig. 1A; Matsuda et al. 1995). Water samples from the mouth of the river had pH₂₅ values of 7.501 and 7.753. Salinity varied according to the mixing ratio of fresh river water and seawater. The mean $A_{\rm T}$ and $C_{\rm T}$ values were 3540 and 3489 μ mol kg⁻¹, respectively (Table 1; Fig. 2A).

Beach water

The salinity of beach water samples was lower than offshore seawater. Salinity declined with increasing distance from the river mouth of the Todoroki and Miyara Rivers, indicating the significant influence of ground water inputs from many seepages along the beach—sea interface. The pH₂₅ ranged between 7.648 and 8.101, averaging 7.897. $A_{\rm T}$ and $C_{\rm T}$ ranged between 2848 and 4460 µmol kg⁻¹ and between 2572 and 4403 µmol kg⁻¹, respectively (Table 1; Fig. 2A). Dissolved silica concentrations were negatively correlated with salinity (r = 0.83) due to the mixing of ground water and offshore water. On the other hand, phosphate concentra-

Table 1 Water temperature, salinity, pH and A_T in offshore and reef water obtained from the Shiraho fringing reef during the morning and afternoon surveys. C_T and f CO_2 at 25 °C were calculated from measurements of temperature, salinity, A_T and pH at 25 °C

Sample		Latitude	Longitude		Temperature °C	Salinity	pH ₂₅	A_T $\mu mol \ kg^{-1}$	C _T µmol kg ⁻¹	f CO ₂ μatm
	the morning									
Offshore v										
M1	24°	21.23'	124°	15.38′	26.76	34.26	8.076	2253	1987	368
M9	24°	22.31'	124°	15.38′	26.74	34.30	8.083	2240	1972	359
Reef water	r									
M2	24°	21.43'	124°	15.23'	27.55	34.20	8.139	2186	1887	296
M3	24°	21.44'	124°	15.08'	27.57	32.96	8.097	2309	2026	358
M4	24°	21.61'	124°	15.45'	27.69	34.30	8.035	2243	1999	412
M5	24°	21.71'	124°	15.12'	27.91	33.04	8.085	2285	2007	366
M6	24°	21.81'	124°	15.38'	26.74	34.31	8.051	2229	1979	392
M7	24°	22.03'	124°	15.31'	26.69	34.29	8.005	2276	2044	455
M 8	24°	22.09′	124°	15.23'	27.02	33.46	8.054	2235	1984	391
M10	24°	22.36'	124°	15.26'	27.28	33.27	8.061	2295	2033	394
M11	24°	22.56'	124°	15.34'	26.68	34.32	7.986	2231	2012	470
M12	24°	22.65′	124°	15.16′	27.27	33.86	7.943	2784	2535	660
Survey in	the afternoon	,								
Reef water										
A1	24°	21.46′	124°	14.96′	29.75	23.08	8.024	3285	2995	695
A2	24°	21.47'	124°	15.12'	30.59	32.53	8.464	2218	1687	107
A3	24°	21.45'	124°	15.26'	29.50	33.27	8.311	2179	1766	174
A4	24°	21.66′	124°	15.18'	28.93	33.67	8.234	2206	1840	224
A5	24°	21.85'	124°	15.07'	30.56	27.69	8.205	2736	2337	322
A6	24°	21.85'	124°	15.17'	29.69	33.14	8.350	2156	1721	152
A7	24°	21.80′	124°	15.27'	28.75	33.80	8.301	2056	1676	170
A 8	24°	21.93'	124°	15.24'	29.33	33.39	8.278	2187	1795	193
A 9	24°	22.05'	124°	15.12'	30.14	31.15	8.265	2295	1899	216

tions were more rapidly depleted than dissolved silica, which suggests that phosphate concentrations were controlled more by consumption by benthic metabolism than by water mixing. Phosphate still remained in the water samples taken at Sts. N7 and N9, although reef water in most of the Shiraho section, except along the beach, was depleted in nutrients below the limits of analytical detection.

Discussion

The carbon budget of coral reefs can be affected by the properties of water, together with biological processes due to reef organisms. These processes can be represented as changes of $A_{\rm T}$ and $C_{\rm T}$ on the $A_{\rm T}$ - $C_{\rm T}$ diagram (Deffeyes 1965) (Fig. 2).

The distribution of ground water in the Ryukyu Islands has been reported by Matsuda et al. (1995). They showed that Irabu Island (Fig. 1A) is underlain by a freshwater lens (<1% seawater), which has a maximum thickness of 12 m in the central part of the island. The freshwater lens overlies a freshwater-seawater mixing zone (1–90% seawater), ranging in thickness from 7 m to more than 30 m, with the thickness increasing toward the coast. A similar picture is reported from Kikai Island (Matsuda et al. 1995; Fig. 1A), and this type of ground water distribution is also expected in Ishigaki Island. Ground water samples from Sts. N1 and N2 were spring water which passed through the Ryukyu limestone.

Judging by the salinities (\approx 0), they came from the freshwater lens. On the other hand, ground water sampled at St. N3 near the coast was pumped up from 10 m depth. The salinity of about 5.9% shows that the water came from the freshwater-seawater mixing zone. The St. N3 sample gave maximum $A_{\rm T}$ and $C_{\rm T}$ values of 4189 µmol kg⁻¹ and 4362 µmol kg⁻¹, respectively, which were approximately twice those of offshore water. Freshwater taken from the Todoroki River gave high values of $A_{\rm T}$ and $C_{\rm T}$, which were comparable to the mean values of fresh ground water.

The dissolution of carbonate rises at $A_{\rm T}$ by 2 moles and the $C_{\rm T}$ by 1 mole for each mole of CaCO₃ dissolved, whereas organic carbon degradation raises the $C_{\rm T}$ by 1 mole without any change in the $A_{\rm T}$. If the dissolution of CaCO₃ is mainly responsible for the increase in $A_{\rm T}$ and $C_{\rm T}$ (approximately 3200 and 1600 µmol kg⁻¹), the rest of $C_{\rm T}$ (1600 µmol kg⁻¹) could be ascribed to the CO₂ derived from organic matter decomposition. This suggests that CO₂ production from organic matter degradation is equivalent to that from carbonate dissolution, and explains the observed $A_{\rm T}$ and $C_{\rm T}$ values in the freshwater samples.

Values of fCO_2 for freshwater samples were calculated to be 3400 μ atm. Ground water sampled at St. N3 displayed extremely high fCO_2 (6435 μ atm), approximately 20 times higher than that of offshore water (364 μ atm). Since the fCO_2 is much higher near the beach than in the atmosphere, CO_2 should be released into the atmosphere.

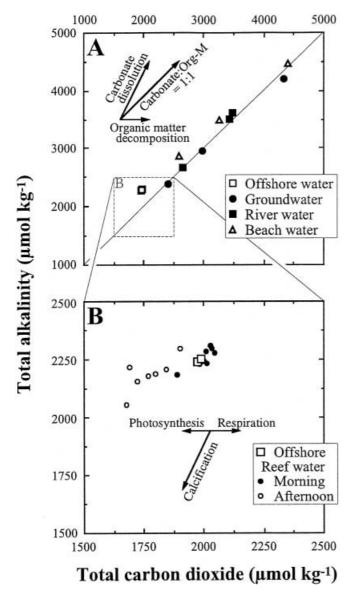


Fig. 2 Total alkalinity (A_T) versus carbon dioxide (C_T) diagram for the Shiraho and Todoroki sections of Ishigaki Island (**A**), and for the offshore and reef flat in the same area during the morning and afternoon of 23 and 24 June 1997 (**B**)

Two biological processes dominate the carbon budget of the coral reef ecosystem: organic carbon metabolism (photosynthetic fixation and respiration/degradation) and inorganic carbon reactions (precipitation and dissolution of calcium carbonate). The contribution of planktonic primary production to shallow reef metabolism is negligible (Kinsey 1985). The fCO_2 in reef waters ranged from 297 to 600 μ atm, averaging 410 μ atm, during the morning survey (Table 1). The elevated fCO_2 is ascribed to an accumulated respiration/degradation effect during the night. In contrast, during the afternoon survey, most of the samples with salinities of 31.15 to 33.80 showed reduced A_T and C_T and correspondingly lower fCO_2 values ranging from 107 to 224 μ atm (Table 1). This decrease in A_T and C_T is presumably the

result of photosynthesis during the day and the residence time (\sim 13 h) of seawater on the reef flat. The seawater properties measured during the 2 days in June 1997 were within the range of diurnal change reported previously from the Shiraho fringing reef (e.g., Suzuki 1995; Suzuki et al. 1995; Kayanne et al. 1995).

On the other hand, two less saline samples taken during the afternoon (A1 and A5) with significant amounts of ground water had high A_T and C_T values with high fCO_2 . The difference must be due to the large contribution of freshwater, because ground water (av. $A_{\rm T} = 3161$, $C_{\rm T} = 3260~\mu{\rm mol~kg}^{-1}$) exhibits higher alkalinity and carbon than offshore seawater (av. $A_T = 2247$, $C_{\rm T} = 1980 \; \mu {\rm mol} \; {\rm kg}^{-1}$). Although $A_{\rm T}$ and $C_{\rm T}$ should be reduced by photosynthesis and calcification during the daytime, less saline beach water showed much higher $A_{\rm T}$, $C_{\rm T}$ and $f{\rm CO}_2$ than the offshore water. Here we present CO₂ data for only 1 day, but the residence time of ground water is several months, and this source of freshwater is frequently responsible for less saline beach water. Therefore, it is plausible that relatively high values of A_T , C_T and fCO_2 occur during the entire year in beach water on the Shiraho fringing reef.

Effects of freshwater on the carbon budget of coral reef ecosystem

Many coral reefs often have little excess primary production (Kinsey 1985) because they are surrounded by tropical oligotrophic (nutrient-poor) ocean, and a low supply of new nutrients is expected to limit production (Crossland et al. 1991). In fact, the phosphate and nitrate concentrations of surface water in the Kuroshio current are below the detection limit (<0.02 μmol lg⁻¹) around the Ryukyu Islands (Watanabe et al. 1995). On the other hand, nutrient-rich freshwater contributes 0.5–1.2% of the water volume to the Shiraho fringing reef/Kawahata et al. 1998). Therefore, appreciable amounts of terrestrial input will modify the carbon budget of this fringing reef.

The median C:N:P atomic ratio of benthic marine macroalgae and seagrass from tropical coastal areas, including coral reefs, is about 550:30:1 (Atkinson and Smith 1983). This is very different from the Redfield ratio of 106:16:1 for phytoplankton (Redfield et al. 1963). Fenchel and Jørgensen (1977) stated that the C:N ratio of benthic plants ranges from 10:1 to 70:1 and that the C:P ratio is about 200:1. Thus, in comparison to phytoplankton, benthic plants are much more depleted in P, and somewhat more depleted in N relative to C. When terrestrial water delivers nutrients to coral reefs, benthic plants can fix CO₂ by photosynthesis and decrease fCO₂. On the other hand, CO₂ dissolved in terrestrial water is transported onto reefs and raises fCO_2 . Therefore, the effects of terrestrial inputs on the net carbon budget in coral reefs depend on the C:P ratios in terrestrial water. When the ratio is smaller than that of the benthic plants (Approximately 550:1), they may

Table 2 Water temperature, salinity, pH and $A_{\rm T}$, phosphate and silica in fresh or low saline water near the Shiraho reef during June 1997
C _T and fCO ₂ at 25 °C were calculated from the measurements of temperature, salinity, A _T and pH at 25 °C

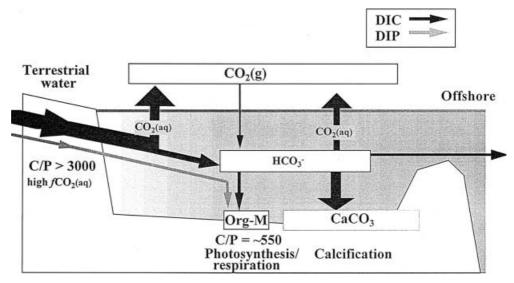
Station	Temperature (°C)	Salinity	pH ₂₅	$A_{\rm T}$ µmol kg ⁻¹	C _T µmol kg ⁻¹	fCO ₂ μatm	Phosphate µmol kg ⁻¹	Silica µmol kg ⁻¹	CT/PO ₄
Ground water									
Spring (N1)	24.4	0.33	7.493	2934	2793		0.34	145	8790
Cave (N2)	23.9	0.32	7.451	2359	2421	2472	0.62	153	3896
Underground water (N3)	25.1	5.92	7.318	4189	4362	6435	1.22	173	3581
River water									
Todoroki river (N4)	27.7	0.26	7.613	2648	2663	1910	0.35	198	7583
Rivermouth water									
Todoroki river mouth (N5)	28.9	10.93	7.753	3588	3516	1845	0.10	124	35309
Miyara river mouth (N6)	28.1	23.99	7.501	3492	3461	2797	0.72	162	4808
Beach water									
Observation site (N7)	29.8	25.01	8.101	2848	2572	481	0.08	28	_
Observation site (N8)	27.0	27.31	7.648	4460	4403	2446	0.28	73	_
Observation site (N9)	30.0	25.01	7.942	3483	3257	909	0.08	63	

absorb all dissolved CO_2 by photosynthesis during the day and the reef will act as a sink for CO_2 . But when terrestrial water inputs have a higher C:P than the plants (i.e. > 550:1), it will raise fCO_2 in the seawater (Atkinson and Smith 1983).

Ground water and river water from Ishigaki Island have high C:P ratios, ranging between 3600 and 35000 (Table 2): several times to two orders higher than those of benthic plants. These inputs will supply a large quantity of C relative to P into the Shiraho fringing reef and raise fCO_2 even during the day, consequently leading to release of CO2 into the atmosphere near the beach. During the night, both respiration and terrestrial CO₂ inputs should enhance the release of CO₂ to the atmosphere (Fig. 3). Even though there is a tight connection between calcification and photosynthesis (e.g., Suzuki. et al 1995), it is widely accepted that calcification plays an important role in the net carbon budget of coral reef ecosystems. This view has been confirmed by investigations conducted on atolls and barrier reefs with lagoons, where the residence time of water is long enough for organic matter to be decomposed (Smith and Pesret 1974; Smith and Jokiel 1978; Kawahata et al. 1997, 1999). The Shiraho reef was a source of CO₂ at the time of this study. Such a situation is likely to prevail all year round, and it may occur elsewhere. Our results provide one of the best examples that the concept of reefs as sources of CO₂ may extend to fringing reefs, which receive more land-derived material than do atolls and barrier reefs. Further investigation is required to generalize the concept to the three types of coral reefs: fringing and barrier reefs and atolls (Gattuso et al. 1995).

As is the case with many developed tropical islands, the fringing reefs of the Ryukyu Islands are being greatly stressed by human activity. Fertilizer runoff may stimulate primary production on coral reefs, which will cause them to retain more CO₂ (Kayanne 1993). In fact, fertilizers enriched in nitrogen, phosphorus and potassium are applied at the rate of 700 kg ha⁻¹ year⁻¹ in the intensive farming (e.g., rice and sugar cane) of Ishigaki Island (Yaeyama Agricultural Agency, personal communication). Ecological studies of the coral reefs around Ishigaki Island may demonstrate that higher nutrient inputs modify the community structure and distribution

Fig. 3 Schematic diagram of the carbon cycle on the Shiraho fringing reef. Ground water and river water show high C:P ratios 7 to 70 times higher than those of benthic plants. Degassing of CO₂ could occur near the beach. Calcification plays an important role in the net carbon cycle, especially on the reef crest. Although phosphate is consumed to produce organic matter in the reef flat during the day, organic matter is quickly decomposed to CO₂ as indicated by very low organic content in the reef sediments. The Shiraho fringing reef system therefore works as a source of CO₂ to the atmosphere



of coral and other benthic organisms as observed in Kaneohe Bay, Hawaii (Smith et al. 1981) and Moorea, French Polynesia (Gattuso et al. 1997). However, judging by the water properties of the ground water and Todoroki and Miyara Rivers of Ishigaki Island, inputs of terrestrial dissolved material enriched in CO₂ relative to phosphate still exceed the anthropogenic nutrient supply around the Shiraho fringing reef.

Acknowledgements We thank S.V. Smith and another reviewer for their comments on the manuscript. We also express our appreciation to K. Goto for the water analysis, to K. Nagayoshi for drawing figures and to H. Yamamoto and Y. Suzuki for assistance in the field. This study was supported by STA and EAJ.

References

- Atkinson MJ, Smith SV (1983) C: N: P ratios of benthic marine plants. Limnol Oceanogr 28: 568-574
- Buddemeier RW (1996) Coral reefs and carbon dioxide. Science 271: 1298–1299
- Crossland CJ, Hatcher BJ, Smith SV (1991) Role of coral reefs in global ocean production. Coral Reefs 10: 55–64
- Deffeyes KS (1965) Carbonate equilibria: a graphic and algebraic approach. Limnol Oceanogr 10: 412–426
- Dickson AG (1993) pH buffers for seawater media based on the total hydrogen concentration scales. Deep Sea Res 40: 107–118
- Fenchel TM, Jørgensen BB (1977) Detritus food chains of aquatic ecosystems: the role of bacteria. Adv Microb Ecol 1: 1–58
- Foster HL (1965) Geology of Ishigaki-shima, Ryukyu-retto. Geol Surv Prof Paper 399-A, p 119
- Frankignoulle M, Canon C, Gattuso J-P (1994) Marine calcification as a source of carbon dioxide: positive feedback of increasing atmospheric CO₂. Limnol Oceanogr 39: 458–462
- Frankignoulle M, Gattuso J-P, Biondo R, Bourge I, Copin-Montegu G, Pichon M (1996) Carbon fluxes in coral reefs. 2. Eulerian study of inorganic carbon dynamics and measurement of air-sea CO₂ exchange. Mar Ecol Prog Ser 145: 123–132
- Gattuso J-P, Pichon M, Delesalle B, Frankignoulle M (1993) Community metabolism and air-sea CO₂ fluxes in a coral reef ecosystem, (Moorea, French Polynesia). Mar Ecol Prog Ser 96: 259–267
- Gattuso J-P, Pichon M, Frankignoulle M (1995) Biological control of air-sea CO₂ fluxes: effect of photosynthetic and calcifying organisms and ecosystems. Mar Ecol Prog Ser 129: 307–312
- Gattuso J-P, Payri CE, Pichon M, Delsalle B, Frankignoulle M (1997) Primary production, calcification and air-sea CO₂ fluxes of a macroalgal-dominated coral reef community (Moorea, French Polynesia). J Phycol 33: 729–738
- Gattuso J-P, Frankignoulle M, Smith SV, Ware JR, Wollast R (1996a) Coral reefs and carbon dioxide. Science 271: 1298
- Gattuso J-P, Pichon M, Delesalle B, Frankignoulle M (1996b) Community metabolism and air-sea CO₂ fluxes in a coral reef ecosystem, (Moorea, French Polynesia). Mar Ecol Prog Ser 145: 109–121
- Kayanne H (1993) Coral reef eco-factory for fixing CO₂. Now Future 8: 11–15
- Kayanne H, Suzuki A, Saito H (1995) Diurnal changes in the partial pressure of carbon dioxide in coral reef water. Science 269: 214–216
- Kawahata H, Suzuki A, Goto K (1997) Coral reef ecosystem works as a source of atmospheric CO₂: evidence from PCO₂ mea-

- surements of surface of Palau Barrier Reef and Majuro Atoll, Western Pacific Ocean. Coral Reefs 16: 261–266
- Kawahata H, Saito I, Suzuki A (1998) Terrestrial inputs potentially influence carbon cycle and metabolism in the Shiraho reef. In Techno-Ocean '98 Organizing Committee, (eds.), Proc Techno-Ocean '98 Int Symp, Kobe, pp 381–384
- Kawahata H, Suzuki A, Goto K (1999) PCO₂ spatial distribution in coral reefs of Majuro Atoll, Marshall Islands. Geochem J 33: 295–303
- Kinsey DW (1985) Metabolism, calcification and carbon production. I Systems level studies. Proc. 5th Int Coral Reef Symp 4: 505–526
- Matsuda H, Tsuji Y, Honda H, Saotome J (1995) Early diagnesis of Pleistocene carbonates from a hydrogeochemical point of view, Irabu Island, Ryukyu Island: porosity changes related to early carbonate diagnesis. In: Budd DA, Saller AH, Harris PM (eds) Unconformities and porosity in carbonate strata. Mem Am Assoc Geol 63: 350–354
- Millero FJ (1979) The thermodynamics of the carbonate system in seawater. Geochim Cosmochim Acta 43: 1651–1661
- Millero FJ, Poisson A (1981) International one-atmosphere equation of state for sea water. Deep-Sea Res 28: 625–629
- Redfield AC, Ketchum BH, Richards FA (1963) The influence of organisms on the composition of sea water. In: Hill MN (ed) The sea, vol 2. Wiley, New York, pp 26–77
- Smith SV (1995) Reflections on the measurement and significance of carbon metabolism on coral reef. Kansas Geological Survey Open-File Report Series 95-56 (Informal communications of SCOR working group 104) Kansas Geological Survey, Kansas, USA, pp 18
- Smith SV, Pesret F (1974) Process of carbon dioxide flux in the Fanning Island lagoon. Pacific Sci 28: 225–245
- Smith SV, Jokiel PL (1978) Water composition and biogeochemical gradients in the Canton Atoll lagoon. Atoll Res Bull 221: 15–53
- Smith SV, Kimmerer WJ, Laws EA, Brock RE, Walsh TW (1981) Kaneohe Bay sewage diversion experiment: perspectives on ecosystem responses to nutritional perturbation. Pacific Sci 35: 279–397
- Strickland JDH, Parsons TR (1972) A practical handbook of seawater analysis. Fish Res Bd Can Bull 167: 1–310
- Suzuki A (1994) Seawater CO₂ system and its transformation caused by photosynthesis and calcification in coral reefs theory and measurements of reef metabolisms. Bull Geol Surv Japan 45: 573–623 (in Japanese with English abstract)
- Suzuki A (1995) Carbon cycle in the coral reef ecosystem. Unpublished PhD Thesis, Tohoku University, Japan, 141pp
- Suzuki A, Kawahata H (1999) Partial pressure of carbon dioxide in coral reef lagoon waters: comparative study of atolls and barrier reefs in the Indo-Pacific Ocean. J Oceanography 55: 731–745
- Suzuki A, Nakamori T, Kayanne H (1995) The mechanism of production enhancement in coral reef carbonate systems: model and empirical results. Sed Geol 99: 259–280
- Suzuki A, Kawahata H, Goto H (1997) Reef water CO₂ system and carbon cycle in Majuro Atoll, the Marshall Islands in the Central Pacific. Proc 8th Int Coral Reef Symp 1: 971–976
- Ware JR, Smith SV, Reaka-Kudla ML (1992) Coral reefs: sources or sinks of atmospheric CO₂? Coral Reefs 11: 127–130
- Watanabe Y, Abe J, Kusakabe M (1995) Characteristics of the nutrients distribution in the East China Sea. In: Tsunogai S, et al. (eds) Proc 1994 Sapporo IGBP Symp, pp 54–60
- Weiss RF (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar Chem 2: 203–215
- Yamamuro M, Kayanne H, Minagawa M (1995) Carbon and nitrogen stable isotopes of primary producers in coral reef ecosystem. Limnol Oceanogr 40: 617–621